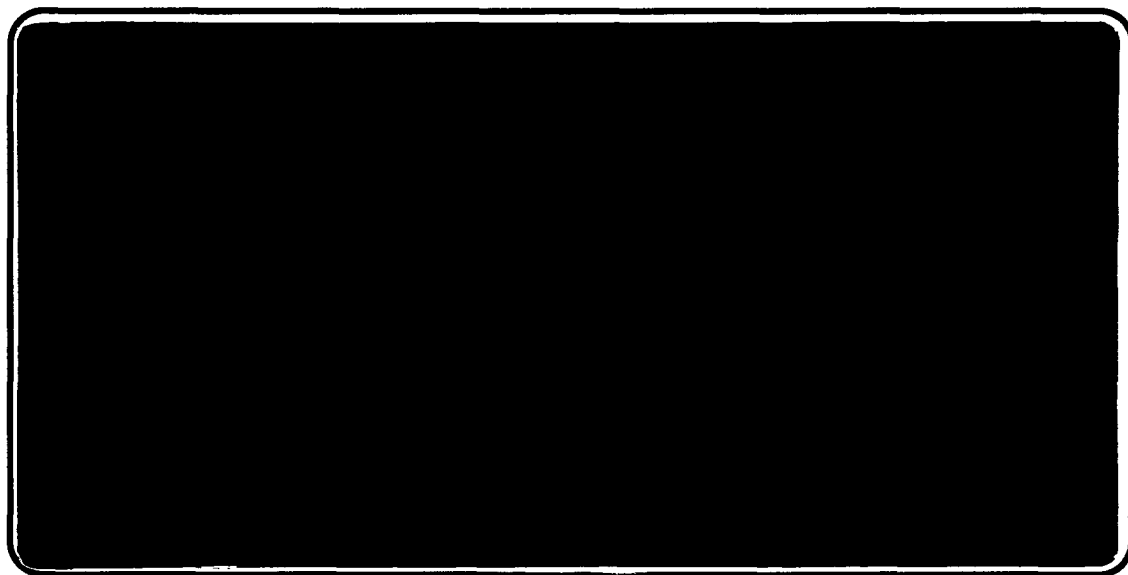




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**INTERPRETING MULTICOMPONENT INFRARED SPECTRA
BY DERIVATIVE MINIMIZATION**

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INTERPRETING MULTICOMPONENT INFRARED SPECTRA BY DERIVATIVE MINIMIZATION

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ABSTRACT

The complexity of a multicomponent spectrum decreases as constituents are removed from it. This decrease is reflected by a reduction in intensity of the first derivative. If the spectrum of a potential constituent is subtracted stepwise from the multicomponent spectrum and a derivative taken at each stage, then the constituent will be identified and factored out if the derivative minimizes.

Stripping a constituent from a multicomponent spectrum reduces the intensity of the residual, and most interpretive schemes attempt to factor out intensities associated with various known components (1-8). A useful algorithm for doing this objectively has been described by Gillette and Koenig (1, 2).

When a constituent is removed from a multicomponent spectrum, the number of bands in the spectrum usually declines, i.e., the complexity of the residual decreases. Consider the spectrum in Fig. 1A which comprises two signals and its derivative. As one of the signals is progressively removed, the absolute value of the overall intensity (positive and negative) of the first derivative decreases until the signal is exactly stripped out in Fig. 1B. Further stripping of the signal increases the intensity of the derivative (Fig. 1C). Thus, the derivative, which relates more closely to spectral complexity than to the intensity, minimizes when a component is exactly removed. Hence, in principle, the intensity of the derivative can be used as a tool for identifying component spectra.

A complication arises if a signal very similar to a constituent is stripped. In Fig. 1D, a signal that is identical to a component signal, but displaced just slightly from it, is subtracted. The intensity of the derivative minimizes as before, although to a lesser extent. However, the likelihood of a noncomponent signal giving rise to a minimum decreases as the complexity of the signals increases, since in all likelihood, a simplification

in one spectral region will be offset by increased complexity in another. Thus, the technique is best suited to spectra rich in detail rather than to broad unstructured bands.

Consider the spectrum in Fig. 2A which contains components from Figs. 2B and 2C. A computer program was written to subtract various fractions (n) of the Fig. 2B spectrum from Fig. 2A and to take a derivative after each stage. A plot of the absolute integrated intensity (positive and negative) of the derivative is plotted against n in Fig. 3. The minimum occurs at $n=0.85$, indicating that 85% of the Fig. 2B spectrum is contained in Fig. 2A. A similar analysis (Fig. 4) shows that 24% of the Fig. 2C spectrum is contained in Fig. 2A.

In summary, the procedure is able to automatically and objectively interpret a complex spectrum without prior knowledge of any of its components. The procedure utilizes all the information in the region where the multi- and pure-component spectra overlap. It is unnecessary for a signal in the mixture to be associated exclusively with any pure-component band; i.e., no restrictions are placed regarding overlapping pure-component bands. Unlike conventional subtraction schemes where one component is scaled and factored out before analysis of another is attempted, our scheme separately considers each pure-component spectrum against the original multicomponent spectrum. Thus, the progressive uncertainty of subtractions are removed.

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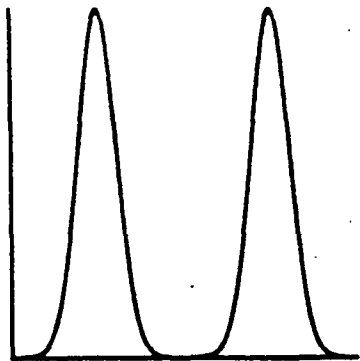
CAPTIONS TO FIGURES

Fig. 1 Gaussian signals and their derivatives. A: 2 equivalent Gaussians. B-D: Residuals after (B) stripping out a component signal; (C) overstripping a component signal; (D) stripping a signal displaced slightly from a component signal.

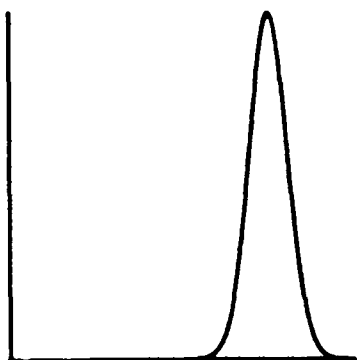
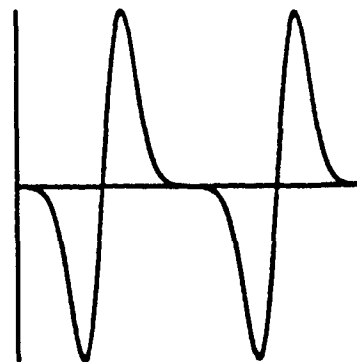
Fig. 2 Spectrum of a mixture (A) including components from (B) and (C).

Fig. 3 Integrated absolute intensities (positive and negative) of derivatives of the Fig. 2A spectrum taken after stepwise subtraction of n times the Fig. 2B spectrum.

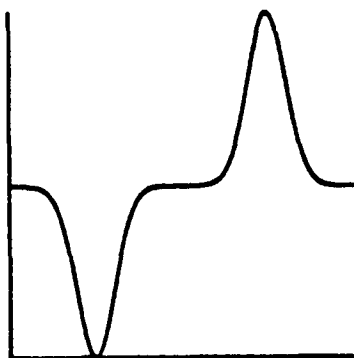
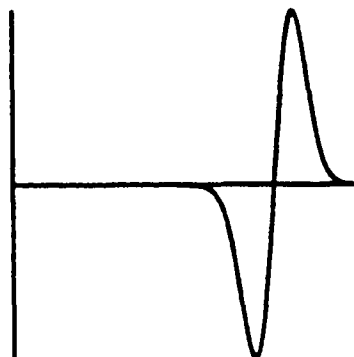
Fig. 4 Integrated absolute intensities (positive and negative) of derivatives of the Fig. 2A spectrum taken after stepwise subtraction of n times the Fig. 2C spectrum.



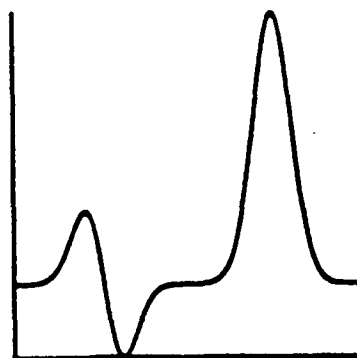
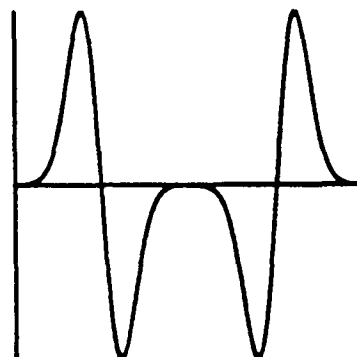
A



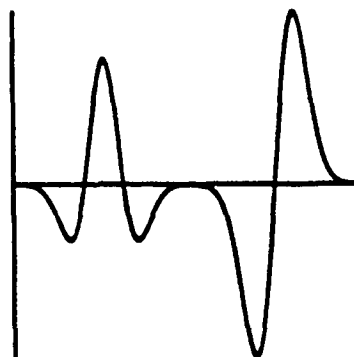
B



C



D



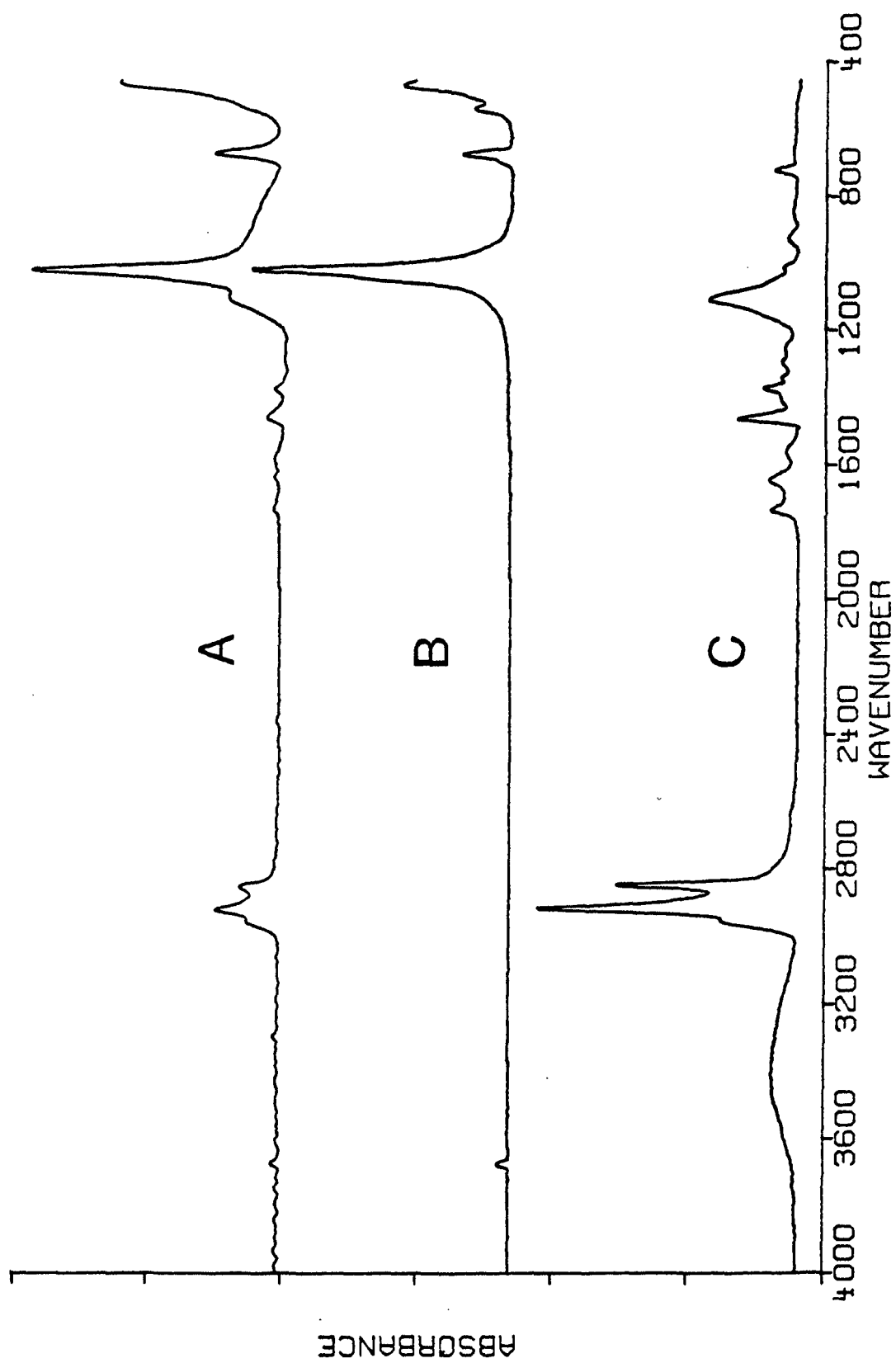


FIG 2

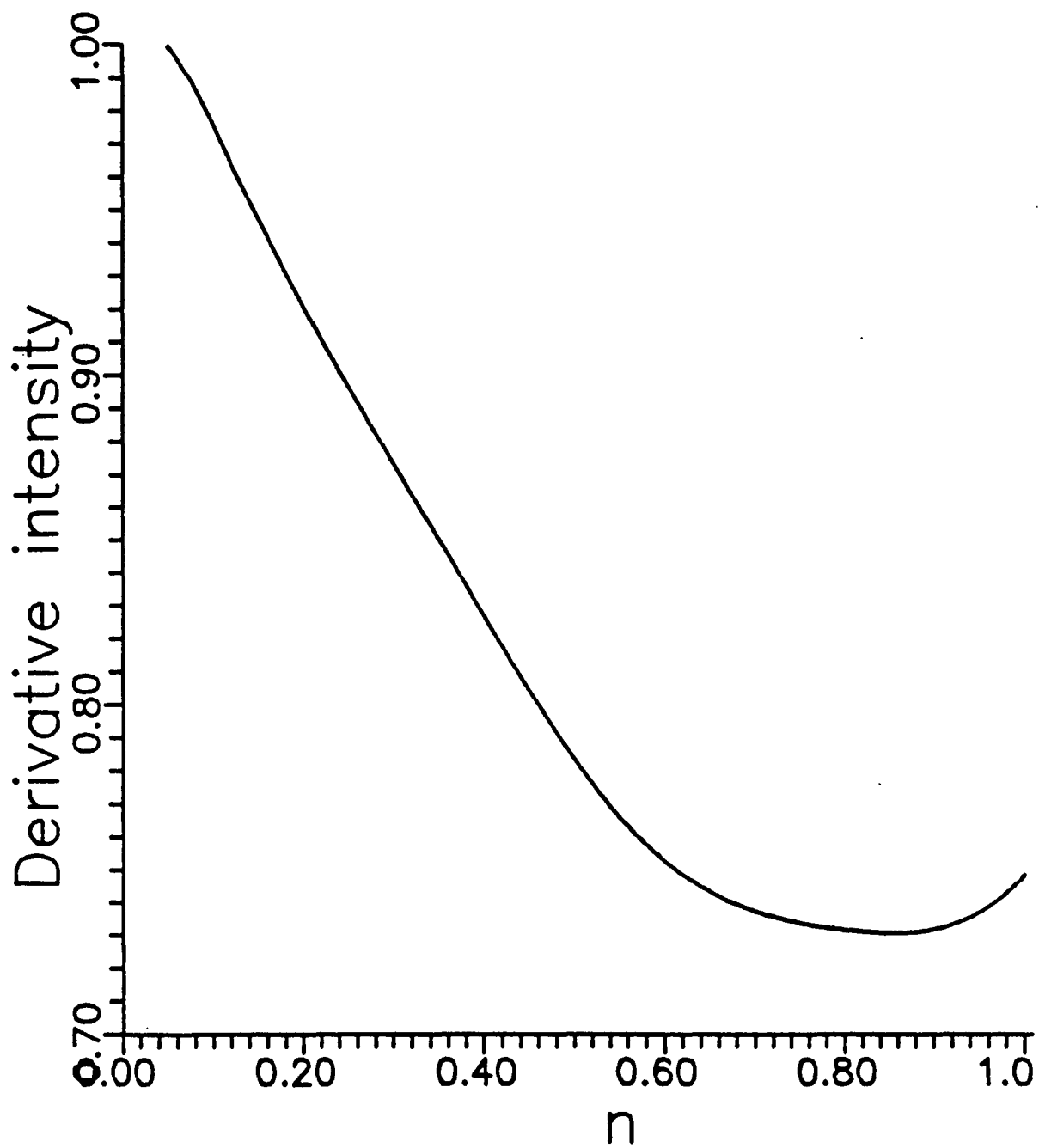


FIG 3

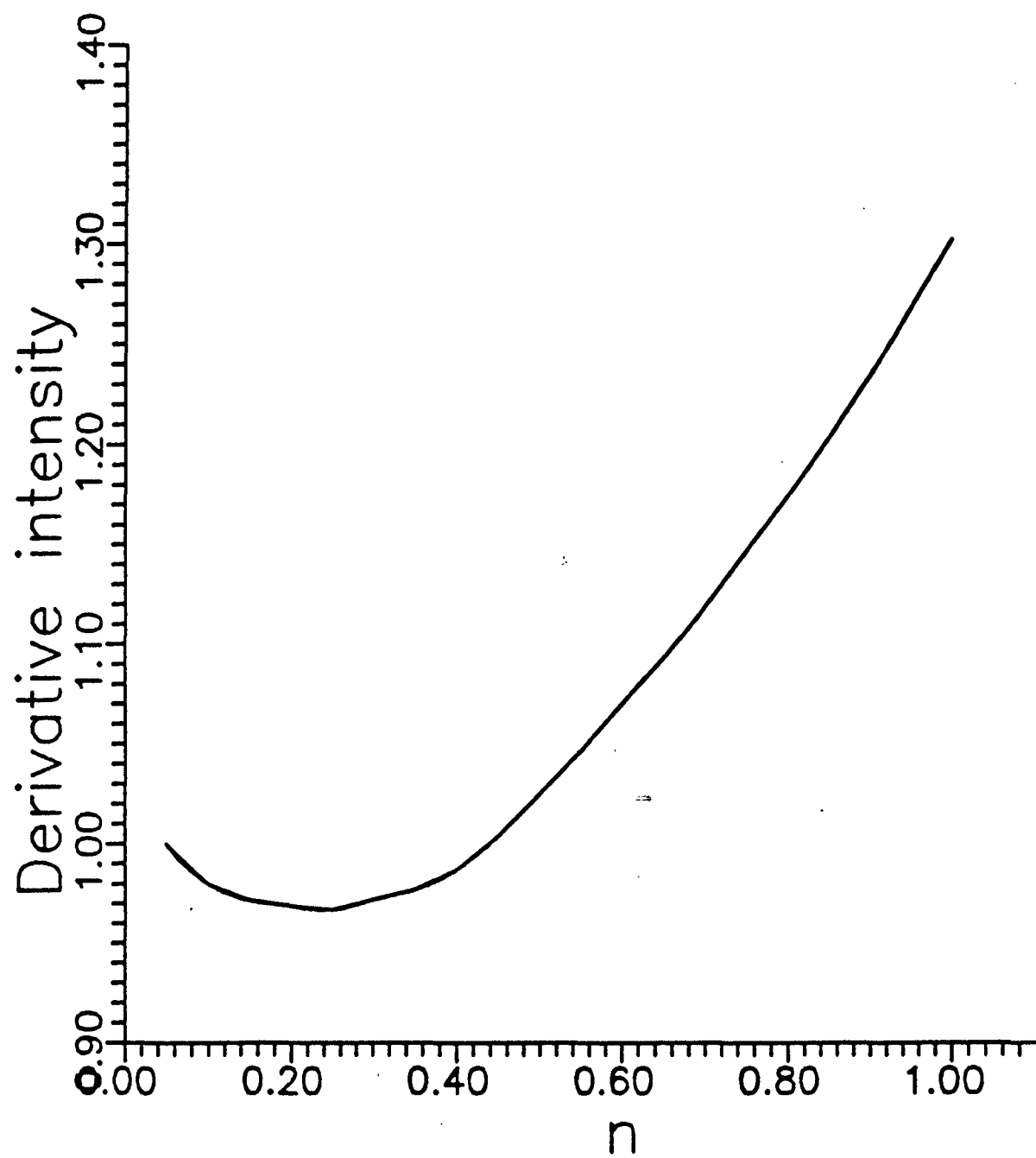


FIG 4